PATENT SPECIFICATION

(11) 1329 815

NO DRAWINGS

(21) Application No. 22558/71 (22) Filed 19 April 1971

(31) Convention Application No. P 20 08 675.3

(32) Filed 25 Feb. 1970 in

(33) Germany (DT)

(44) Complete Specification published 12 Sept. 1973

(51) International Classification C07C 33/04 C07D 29/16

(52) Index at acceptance

C2C 3A13A1A1 3A13A1A2 3A13A1A4 3A13A1K 3A13A3A1C 3A13A3B1 3A13A3C

(19)

1329815

(54) PRODUCTION OF TERTIARY ACETYLENIC GLYCOLS BY REACTION OF ACETYLENE WITH KETONES

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German joint stock company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of tertiary acetylenic glycols by reaction of acetylene with ketones.

There are several valuable methods for the production of acetylenic monoalcohols according to which aldehydes and ketones are reacted with acetylene in the presence of basic substances, such as basic ion exchangers or alkali metal hydroxides, in solvents such as liquid ammonia, tetrahydrofuran and dimethylformamide. In some cases only catalytic amounts of the basic substances are required.

No similar advantageous methods of production are known for acetylenic glycols.

According to the Reppe ethynylation processes with copper acetylide as a catalyst, lower aldehydes such as formaldehyde and acetaldehyde may be reacted readily with acetylene to form the corresponding acetylenic monoalcohols and acetylenic glycols, but in the case of higher aldehydes these methods do not result in yields which are adequte for industrial exploitation. These methods are not suitable for the reaction of ketones with acetylene.

In the direct reaction of 2 moles of ketone with 1 mole of acetylene, at least 1 mole of the basic condensing agent is necessary (Tedeschi, J. Org. Chem., 30 (1965), pages 3045 to 3049).

According to the said literature reference, the reaction of 2 moles of acetone for example with 1 mole of acetylene proceeds best when using solvents such as acetals or ethers in the presence of at least one mole of potassium hydroxide.

$$\underset{CH_3}{\overset{CH_3}{C}}=O+HC\equiv CH+O=\underset{CH_3}{\overset{CH_3}{C}}-KOH\rightarrow HO-\underset{CH_3}{\overset{CH_3}{C}}-C\equiv C-\underset{CH_3}{\overset{CH_3}{C}}-OH.KOH$$

A slight excess of potassium hydroxide (from 10 to 20%) is necessary. The amount of water in the potassium hydroxide determines the consumption of potassium hydroxide.

Good results can only be achieved however with a finely divided, particularly effectively dehydrated, 98 to 99% potassium hydroxide powder.

According to Bergmann *et al* (J. Appl. Chem. (1953), page 40) the use of a commercial-grade potassium hydroxide powder containing about 15% of water in methylal as a solvent gives a yield of only 0.425 mole of tetramethylbutynediol per mole of potassium hydroxide. Similar results are obtained by following the teaching of U.S. Patent No. 3,462,507.

If the reaction is carried out in xylene as a solvent, and a commercial-grade potassium hydroxide powder having a water content of 12% is used, only 0.25 mole of tetramethylbutynediol is obtained per mole of KOH according to German Printed Application No. 1,101,404, Example 2.

Moreover, when potassium hydroxide powders are used, the reaction mixture is often so viscous that mixing in conventional stir-

[*Price 25p*]

red vessels is no longer possible and either special stirring equipment has to be used or the mixture has to be made capable of being stirred by a large excess of solvent.

We have now found that the production of tertiary acetylenic glycols by reaction of a ketone with acetylene in an aliphatic, cycloaliphatic or aromatic hydrocarbon as solvent can be carried out with particular advantage by effecting the reaction in the presence of a potassium alcoholate of a primary or secondary alcohol which has limited solubility in water, i.e. an alcohol of which at 20°C a maximum of not more than 30 g dissolved in 100 g of water. Desirably, a maximum of from 5 to 20 g of the alcohol dissolves in 100 g of water at 20°C.

Examples of suitable alcoholates are potassium alcoholates of primary alcohols such as n - butanol, isobutanol, n - pentanol, 2-methylbutanol - 4, 2 - methylbutanol - 1, 2,2 - dimethylpropanol - 1, n - hexanol, and 2 - ethylhexanol, and also potassium alcoholates of secondary alcohols such as butanol-2, pentanol - 2, pentanol - 3, 2 - methylbutanol - 3 and cyclohexanol.

In the case of these alcohols having limited solubility in water the potassium alcoholates may for example be readily obtained by boiling an aqueous caustic potash solution (for example a commercial 50% aqueous caustic potash solution) with an excess of alcohol under reflux, separating the lower aqueous layer from the two-phase azeotrope with water forming at the top of a fractionating column, and returning the alcohol to the column as a reflux. A solution of the desired potassium alcoholate is thus obtained in a short time. After a hydrocarbon having a higher boiling point than the alcohol used has been added, the excess alcohol is distilled off. There remains a potassium alcoholate devoid of alcohol which is partly suspended in the hydrocarbon and partly dissolved. It is also possible however to remove first the water (as an azeotropic mixture with the alcohol) from the mixture of aqueous caustic potash solution and excess alcohol and then the excess alcohol and to suspend the potassium alcoholate thus obtained in the solvent.

Hydrocarbons suitable as solvents include aliphatic, cycloaliphatic or aromatic hydrocarbons having a boiling range of from 60° to 200°C, particularly from 80° to 180°C, or mixtures of these hydrocarbons. It is preferred to use gasoline mixtures as aliphatic hydrocarbons, cyclohexane as a cycloaliphatic hydrocarbon, and benzene, toluene, xylene, cumene or *p* - isopropylbenzene as aromatic hydrocarbons.

Aliphatic ketones such as acetone, methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, ethyl propyl ketone, ethyl hexyl ketone, araliphatic ketones such as acetophenone, methyl benzyl ketone and benzophenone, cycloaliphatic ketones such as cyclohexanone and cyclopentanone, and heterocyclic ketones such as piperidone - (4) and pyrrolidone-(2) which may bear hydrocarbon radicals, preferably alkyl radicals, as substituents, such as 1,2,2,5 - tetramethylpiperidone - (4), are suitable for the production of acetylene glycols. Ketones of higher molecular weight, for example hexahydrofarnesylacetone containing eighteen carbon atoms, may however also be used as starting materials. It is only α,β-unsaturated ketones such as methyl vinyl ketone or β - ionone which are unsuitable because these often tend to undergo polymerization or autocondensation under the reaction conditions.

In carrying out the process it is advantageous to introduce the ketone into the suspension of the potassium alcoholate in a hydrocarbon at a temperature of from 10° to 80°C, preferably from 20° to 50°C, and at the same time to pass acetylene through the reaction mixture, i.e. to saturate the solution with acetylene.

Soon after introduction of the carbonyl compound has been completed the introduction of acetylene is also stopped and the reaction mixture is stirred well with water. Reaction mixtures are obtained which can be stirred well in standard stirred vessels. About 2 liters of water is used per kg of 100% KOH so that an about 33% aqueous caustic potash solution is formed. Two layers form.

The lower layer of aqueous caustic potash solution contains practically no acetylenic glycol. The upper organic layer is neutralized to pH 5 to 6 with acid and then the solvent is recovered therefrom by distillation. The solvent is free from water and may be reused immediately in the reaction. The acetylenic glycol is advantageously purified by vacuum distillation.

If the ketone used has very little tendency to undergo autocondensation, as is the case for example with methyl ethyl ketone and most of the said ketones, the 30% aqueous caustic potash solution may also be reused for the production of potassium alcoholate.

From 0.8 to 0.9 mole of acetylenic glycol is obtained per mole of KOH (pure substance). This process is therefore very advantageous industrially, especially since the potassium alcoholate can be obtained from aqueous caustic potash solution, the 30% aqueous caustic potash solution obtained in the reaction can be reused for the preparation of the potassium alcoholate and readily accessible hydrocarbons may be used as solvents.

The acetylenic glycols prepared by the process according to the invention are intermediates for further synthesis. For example dimethylhexynediol obtained according to Example 1 is a starting material for chrysanthemum carboxylic acid which is the fundamental compound for insecticides of the

pyrethrum group which are nontoxic to warm-blooded animals. The dimethyloctynediol prepared according to Example 2 may be further processed into perfumes similar to terpenes. The decynediol of Example 3 may be used direct as a surfactant having low lather. Finally reaction of the acetylenic glycols with hydrogen peroxide gives hydroperoxides which may be used as initiators for polymerization by the free radical mechanism.

The invention is illustrated by the following Examples, in which parts are by weight.

EXAMPLE 1

10 parts of 50% aqueous caustic potash solution (0.89 mole) and 30 parts of isobutanol are boiled while stirring in a vessel connected to a downstream distillation column.

The azeotropic mixture occurring at the top of the column (isobutanol and water) separates into two layers. The lower aqueous layer is separated and the isobutanol layer is returned to the separating column as a reflux. In two to three hours, about 6 parts of water is separated and thereafter aqueous isobutanol is distilled of which contain about 0.6 part of water. 10 parts of xylene is added to the mixture and during boiling under reflux all the excess isobutanol is removed from the reaction mixture.

About 15 parts of a suspension of potassium isobutylate in xylene remains which flows well when hot. This 15 parts (0.89 mole) of potassium isobutylate is diluted with another 15 parts of xylene in a stirred vessel having an anchor agitator and, after the vessel has been flushed with nitrogen, this suspension is saturated with acetylene at about 30°C.

While continuing to pass acetylene through, 10 parts of acetone is then introduced in the course of five to six hours. The temperature is kept at 30° to 40°C. When all has been fed in, acetylene is passed in for another hour.

The reaction mixture is then stirred with 9 parts of water and the aqueous alkaline layer is separated. The upper organic layer is neutralized to pH 5 with formic acid. After the excess solvent has been distilled off, 10.2 parts (0.72 mole) of 2,5 - dimethylhexyne-(3) - diol - (2,5) is obtained, having a boiling point of 113° to 114°C at 15 mm Hg.

EXAMPLE 2

15 parts of methyl ethyl ketone is introduced in the course of five to six hours into a suspension of 15 parts (0.89 mole) of potassium isobutylate in xylene (prepared from 10 parts of a 50% caustic potash solution according to Example 1) after dilution with another 10 parts of xylene and simultaneous saturation with acetylene as in Example 1.

After the reaction mixture has been worked up, 13.3 parts (0.79 mole) of 3,6 - dimethyloctyne - (4) - diol - (3,6) (boiling point 126° to 128°C at 17 mm Hg) is obtained from the organic layer by distillation; the excess methyl ethyl ketone is recovered.

EXAMPLE 3

9 parts of methyl isobutyl ketone is introduced into a suspension of 15 parts (0.89 mole) of potassium isobutylate (prepared from 10 parts of a 50% caustic potash solution) in xylene with simultaneous passing through of acetylene, the procedure described in Example 1 being followed.

After the reaction mixture has been worked up, 11 parts of 2,4,7,9 - tetramethyldecyne-(5) - diol - (4,7) is obtained (0.6 mole). Boiling point 106° to 108°C at 1 mm Hg.

EXAMPLE 4

680 parts (6 moles) of a 50% aqueous caustic potash solution is boiled together with 3000 parts of n - butanol while stirring in a flask connected to a distillation column. An azeotrope forms at the top of the column which consists of n - butanol and water from which 543 parts is separated as the lower aqueous layer.

n - butanol is then distilled off and, after 1500 parts of xylene has been added, distillation is continued until the temperature of the material distilling over is 133° to 136°C and consequently all excess butanol has been removed from the reaction mixture.

500 parts of acetone is introduced into the remaining suspension at 30°C within five hours while at the same time passing acetylene through.

After 650 parts of water has been added, two layers form. The upper organic layer is neutralized with formic acid and distilled. 520 parts (3.7 moles) of 2,5 - dimethylhexyne - (3) - diol - (2,5) is obtained.

EXAMPLE 5

As described in Example 4, 588 parts of an aqueous 33% caustic potash solution (equivalent to 3.5 moles of KOH) is boiled while stirring with 1500 parts of n - butanol in a flask with an attached distillation column. An azeotrope of n - butanol and water is condensed at the top of the column. About 460 parts of lower aqueous layer is separated from the condensate. Distillation is continued with good reflux until the boiling temperature of anhydrous n - butanol (117°C) is reached at the top of the column. The n - butanol is then distilled off. To remove residual n - butanol the residue remaining in the flask is finally heated to about 150°C at 30 to 60 mm Hg. The remaining powder of potassium butylate is converted into a suspension by adding 1500 parts of cyclohexane.

588 parts of cyclohexanone is introduced into this suspension at 30° to 35°C within four hours while at the same time saturating the suspension with acetylene. Then 390 parts of water is added to the mixture. Two layers form and are separated. The lower aqueous layer is an about 30% aqueous caustic potash solution which may be reacted again with n - butanol to form potassium butylate. The upper organic layer is neutralized with formic acid and the cyclohexane is recovered by distillation.

After the solvent has been distilled off, a residue remains which contains 589 parts of the desired 1,2 - bis - (cyclohexan - (1)-ol - (1) - yl) - ethyne.

The yield is about 88% of the theory based on cyclohexanone. The melting point is 108° to 109°C (recrystallized from carbon tetrachloride).

EXAMPLE 6

A solution of 1100 parts of benzophenone (6 moles) in 700 parts of cumene is added within six hours at 20° to 30°C to a suspension of 502 parts (4.5 moles) of potassium isobutylate (prepared as described in Example 1, but with cumene as solvent) with simultaneous saturation with acetylene.

480 parts of water is added and the aqueous caustic potash solution is separated. The organic layer is neutralized with formic acid and part of the solvent is distilled off at subatmospheric pressure (about 50 mm Hg). The desired 1,1,4,4 - tetraphenyl - 2 - butyn-(1,4) - diol crystallizes out from the solution. Further amounts of crystallized product are obtained by further concentration of the mother liquor.

942 parts of the product is obtained in all.

The yield is about 80% of the theory, based on benzophenone. The melting point is 192°C.

EXAMPLE 7

502 parts (4.5 moles) of powdered potassium isobutylate (prepared as described in Example 5) is suspended in 1000 parts of hexane. A solution of 930 parts of 1,2,2,5-tetramethylpiperidone - (4) in 930 parts of hexane is added to the suspension in the course of five hours at 20° to 35°C, the solution being at the same time saturated with acetylene.

450 parts of water is added and the aqueous caustic potash solution is separated. The organic phase is neutralized with formic acid and the hexane is distilled off.

820 parts of 1,2 - bis - (1,2,2,5 - tetramethylpiperidin - (4) - ol - (4) - yl) - ethyne is obtained as a honey colored substance whose structure is confirmed by infrared analysis.

The yield is 82% of the theory based on 1,2,2,5 - tetramethylpiperidone - (4).

EXAMPLE 8

135 parts of potassium isobutylate (prepared analogously to Example 1) is suspended in 1140 parts of xylene.

Acetylene is passed through the suspension at 35°C and at the same time 536 parts of 2,6,10 - trimethylpentadecanone - (14) (hexahydrofarnesylacetone) is introduced in the course of eight hours.

200 parts of water is added to the reaction mixture and the organic phase is separated from the aqueous caustic potash solution. The organic phase is adjusted to pH 3 to 4 by adding a small amount of formic acid and then the solvent (xylene) is distilled off at 100 mm Hg. 562 parts of an oil containing a small amount of dehydroisophytol is obtained as residue.

1,2 - bis - (6,10,14 - trimethylpentadecan-(2) - ol - (2) - yl) - ethyne is obtained as a transparent oily substance which boils at 180° to 185°C at 0.01 mm Hg.

WHAT WE CLAIM IS:—

1. A process for the production of a tertiary acetylenic glycol by reaction of a ketone with acetylene in an aliphatic, cycloaliphatic or aromatic hydrocarbon as a solvent wherein the reaction is carried out in the presence of a potassium alcoholate of a primary or secondary alcohol of which at 20°C a maximum of not more than 30 g dissolves in 100 g of water.

2. A process as claimed in claim 1 carried out at a temperature of from 20° to 50°C.

3. A process as claimed in claim 1 or 2 wherein benzene, toluene, xylene or *p* - isopropylbenzene is used as solvent.

4. A process as claimed in any of claims 1 to 3 wherein the alcohol of the potassium alcoholate is a compound of which a maximum of from 5 to 20 g dissolves in 100 g of water at 20°C.

5. A process as claimed in any of claims 1 to 3 wherein the alcohol of the potassium alcoholate is n - butanol, isobutanol, n - pentanol, 2 - methylbutanol - 4, 2 - methylbutanol - 1, 2,2 - dimethylpropanol - 1, n - hexanol, 2 - ethylhexanol, butanol - 2, pentanol - 2, pentanol - 3, 2 - methylbutanol-3 or cyclohexanol.

6. A process as claimed in any of claims 1 to 5 wherein the ketone is acetone and 2,5-dimethylhexyne - (3) - diol - (2,5) is produced.

7. A process as claimed in any of claims 1 to 5 wherein the ketone is methyl ethyl ketone and 3,6 - dimethyloctyne - (4) - diol-(3,6) is produced.

8. A process as claimed in any of claims 1 to 5 wherein the ketone is methyl isobutyl ketone and 2,4,7,9 - tetramethyldecyne-(5) - diol - (4,7) is produced.

9. A process as claimed in any of claims

1 to 5 wherein the ketone is cyclohexanone and 1,2 - bis - (cyclohexan - 1 - ol - 1 - yl)-ethyne is produced.

10. A process as claimed in any of claims 1 to 5 wherein the ketone is benzophenone and 1,1,4,4 - tetraphenyl - butyne - (2) - diol - (1,4) is produced.

11. A process as claimed in any of claims 1 to 5 wherein the ketone is 1,2,2,5 - tetramethylpiperidone - (4) and 1,2 - bis - (1,2,2,5-tetramethylpiperidin - 4 - ol - 4 - yl) - ethyne is produced.

12. A process as claimed in any of claims 1 to 5 wherein the ketone is 2,6,10 - trimethylpentadecanone - (14) and 1,2 - bis-(6,10,14 - trimethylpentadecan - 2 - ol - 2-yl) - ethyne is produced.

13. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.

14. Tertiary acetylene glycols when obtained by the process claimed in any of claims 1 to 13.

J. W. & G. W. JOHNSON,
Furnival House,
14—18, High Holborn,
London, WC1V 6DE.
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.